INTERLABORATORY
STUDY 92-4

TRACE
METAL
STANDARD
SOLUTIONS

IN SUPPORT OF

THE INTEGRATED
ATMOSPHERIC
DEPOSITION
NETWORK
(IADN)

JULY 1992

Ⓥ Ontario

█♦█ Environment   Environnement
Canada   Canada

Atmospheric   Service
Environment   de l'environnement
Service   atmosphérique

INTERLABORATORY STUDY 92-4

TRACE METAL STANDARD SOLUTIONS

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THE INTEGRATED ATMOSPHERIC DEPOSITION NETWORK (IADN)

JULY 1992

Report Prepared by

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Environment Canada
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1   SUMMARY OF INTERLABORATORY STUDY 92-4

Interlaboratory Study 92-4 was initiated in support of the Integrated Atmospheric Deposition Network (IADN) to provide an initial assessment of laboratory variability for the analysis of Trace Metals. Participation was limited to laboratories which contribute to the IADN database or related programs. This study was sponsored by the Canada-Ontario Agreement (COA) Air Toxics Workgroup, and conducted as a joint project between the Atmospheric Environment Service (AES) of Environment Canada and the Quality Management Unit (QMU), Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

Eight participating laboratories received a set of four ampouled standards that were ready for direct instrumental analysis. The parameter list consisted of 8 different elements. Results were received from seven laboratories.

The results of this interlaboratory study indicate that the participants have an agreement of $\pm 10\%$ to the target for all elements except Aluminum. The lack of sensitivity for Aluminum analysis suggests that $\pm 30\%$ is the level of agreement achievable at this time. Within-laboratory performance across the concentration range was very consistent, with one or two individual problems for one or two elements. Intercept problems are the most common source of between-laboratory variability. Individual participants may be biased high or low for one or two individual Trace Metals. As between-participant bias may be as high as 20%, the use of a common reference standard could help improve this bias to 5-10%. This would reduce the potential bias from contributing laboratories to the central IADN database.

2   INTRODUCTION

Interlaboratory performance studies are conducted to assess the comparability and accuracy of data among different laboratories. These studies are useful for the identification of biases, precision and accuracy problems. Participation in such studies can serve as a guide for improving individual laboratory performance and maintaining performance standards.

This study was designed to assess the analytical variability among laboratories contributing to the Integrated Atmospheric Deposition Network (IADN). IADN was established as a joint venture between Canada and the United States under the direction of the International Joint Commission[1]. The intent of IADN is to identify toxic airborne substances in the Great Lakes Basin, and by means of the network, quantify the total and net atmospheric loadings of these contaminants, and define spatial and temporal trends in the atmospheric deposition of these substances. Data from several participating agencies is to be merged into a central database. Comparability of these contributing data sets is an important component of the IADN Quality Assurance Implementation Plan[2]. This interlaboratory study provides information to help establish the comparability of data sets and is a recommended activity of the IADN Quality Assurance Program Plan[3]. Sponsorship of this interlaboratory study was through the Canada-Ontario Agreement (COA) Air Toxics Workgroup. Funding for the purchase of materials came from the Atmospheric Environment Service (AES) of Environment Canada. Co-ordination and implementation of the study was done by the Quality Management Unit (QMU) of Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

Interlaboratory Study 92-4 targets laboratories analyzing for Trace Metals in ambient air and/or precipitation. The aim of this study was to establish the comparability of instrumental calibration among the participating laboratories. Each participant received a set of 4 ampouled standards containing eight different elements (Trace Metals) ready for direct instrumental analysis.

A list of participants is given in Appendix 2. Each participant was assigned a unique identification code for ease in data manipulation.

Section 3 describes sample preparation, sample distribution, analytical methodology, and data evaluation procedures. Final results are tabled in Appendix 1 and discussed in Section 4.

3   PROCEDURE

3.1   Preparation of Ampouled Standards

The QMU of LSB, MOEE provided individual concentrated stock solutions of the eight trace metals to be used in this study. These solutions had been previously verified against US-EPA materials and used extensively for LSB in-house Performance Evaluation samples and MOEE interlaboratory studies. Four combined solutions were prepared by diluting aliquots of the concentrated stocks in distilled, deionized water (DDW). Target levels attempted to cover the routine analytical range of most participants. The solutions were preserved with 2% concentrated nitric acid. The solutions were sealed into 50 mL clear ampoules and verified using Inductively-Coupled Plasma/Mass Spectrometry (ICP/MS) analysis by an analyst at LSB not involved in the analysis of ambient

air or precipitation. The ampouled solutions were stored at room temperature until shipped to the participants.

3.2 Sample Distribution

Samples were packed into styrofoam shipping containers and shipped by Purolator Courier to the participating laboratories. A list of the laboratories receiving sample sets is given in Appendix 2. Samples were shipped on July 13, 1992. A copy of all correspondence is also included in Appendix 2.

3.3 Analytical Methodology

Participating laboratories were requested to analyze the samples using their routine in-house methods used to analyze ambient air or precipitation samples for the IADN program. The solutions were intended for direct instrumental analysis and participants were told not to use any digestion or pre-concentration procedures. Participants were requested on the report form provided (Appendix 2) to indicate the Instrument used. All participants were assigned a unique identification code that does not correspond to the order the participants are listed in Appendix 2.

3.4 Data Reporting

Results were submitted to the QMU, LSB in written form. All data were manually entered by laboratory code into an electronic spreadsheet. Participants were not asked to provide replicate results, though several laboratories did provide duplicate or triplicate results or results using two different techniques. For those participants that did provide more than one result using the same analytical technique, a mean value was entered into the Table of Results.

The participating laboratories were mailed a copy of the tables of results on November 4, 1992. No corrections were reported, but there was one revision to the results for Lead. Laboratory 9246 initially provided two sets of Lead and Cadmium results, using both Inductively-Coupled Plasma/Atomic Emission Spectroscopy (ICP-AES) and Graphite Furnace Atomic Absorption Spectroscopy (GFAAS), without indicating which technique was used for the IADN program. The original table of results for Lead contained the ICP-AES values, but samples for the IADN program have Lead analysis done by GFAAS. The ICP-AES Lead values were replaced by the GFAAS Lead values.

The interlaboratory mean, standard deviation (SD), and relative standard deviation (%RSD) were calculated for each Trace Metal and are included in Tables 1-4, Appendix 1.

To easily compare the performance of the participating laboratories, the difference from target for each participant versus target concentration was plotted for each individual Trace Metal. The percent difference from target for each individual Trace Metal was plotted in a similar manner. These graphs are included in Appendix 1.

4   DISCUSSION

OVERVIEW OF INTERLABORATORY PERFORMANCE

Results were received from seven of the laboratories which received the ampouled standards. Comments re difficulties with analyses reported by the participants are noted below in the individual laboratory review. A description of the principles upon which the following discussion is based is provided in Appendix 3.

The results for Aluminum (Figure 1) demonstrate an intercept range of approximately 50 μg/L, excluding Laboratory 9244 (see individual discussion below). Most laboratories demonstrate consistent performance across the analytical range targeted by ampoules IADN2, IADN3 and IADN4. More variable performance is observed at the lowest concentration level (Ampoule IADN1). Laboratories 9245 and 9247 are biased high. The analytical techniques used for Trace Metal analysis are less sensitive for Aluminum as compared to other elements in this study, so that it may be difficult for the participants to improve their performance at lower concentration levels. There is a between-laboratory range of ±20% (Figure 2) that should be improved upon.

The Arsenic results (Figure 3) demonstrate between-laboratory slope-dependant bias. Laboratory 9246 has a high slope bias. The participants demonstrated a between-laboratory range of 20% (Figure 4), excluding Laboratory 9246, though Laboratory 9241A was also high for Ampoule IADN1.

The results for Cadmium (Figure 5) demonstrate slope-dependant bias. Laboratories 9241A and 9248 have low slope biases. The between-laboratory range for the other participants is 15% at the lower concentrations and is very good at 10% for the highest concentration (Figure 6), despite the negative slope biases noted above.

The Chromium results (Figure 7) indicates an intercept dependant bias of approximately 2-5 μg/L. Many of the participants appear to lack sufficient sensitivity for this element at the lowest target concentration in this study. Laboratory 9242 had erratic performance for this element. The between-laboratory range is approximately 40% at the lower concentrations and improves to 20% at the highest concentration (Figure 8), excluding Laboratory 9242.

The interlaboratory performance for Copper (Figure 9) demonstrates a general intercept problem of approximately 3-5 μg/L. Laboratory 9248 also has a negative slope bias of -10%. Excluding Laboratories 9242 and 9244 for Ampoules IADN1 and IADN2, the between-laboratory range is approximately 30% (Figure 10).

The Lead results (Figure 11) indicate an intercept bias of approximately 2 μg/L. Except for Laboratory 9241A (see individual review), the between-laboratory bias is within ±10% (Figure 12).

The results for Selenium (Figure 13) indicate some intercept problems. Laboratory 9246 had erratic performance for this element. The other laboratories demonstrate a between-laboratory range of approximately 20% (Figure 14).

The Zinc results (Figure 15) demonstrate an intercept bias of approximately 5 μg/L, excluding Laboratory 9247. Laboratory 9241 has high positive slope bias. The between-laboratory range was approximately 25% (Figure 16), excluding Laboratories 9241 and 9247 in Ampoule IADN1. Laboratory 9247 may also have had an intercept problem or some contamination in sample IADN1.

Several laboratories have intercept problems which should be investigated. Precipitation and ambient air are expected to have low concentration of Trace Metals. Intercept biases will have a noticeable effect on low level data. By improving on intercept problems, laboratories contributing to the IADN database will reduce the risk of providing biased results to the central database.

The overall performance indicates that the between-laboratory variability for most elements is within ±10% over the concentration range of this study. Several participants had a high or low slope bias on one or two elements. This should be investigated and corrected with the use of a reference standard. While one participant may differ by only +10% from the target, and another by -10% from the target, the two participants differ by 20% with respect to each other. If the two "extreme" laboratories are contributing to the IADN database with a 20% bias between them, this could lead to greater differences in the data sets than desired. By monitoring their in-house standards with a common reference standard, the laboratories contributing to the IADN database should be able to reduce their between-laboratory variability to ±5%. This would result in only a 10% bias between the "extreme" laboratories and improve the comparability of the data being submitted to the central IADN database.

INDIVIDUAL LABORATORY PERFORMANCE

Laboratory 9241

Laboratory 9241 reported results for all parameters except Selenium using ICP-AES but noted that they routinely use GFAAS for low levels of Copper, Lead, Cadmium and Arsenic. Selenium is only done on GFAAS. However, at the time of the study, their GFAAS was broken, so they submitted the ICP-AES results to meet the study deadline of August 7, 1992. In September their GFAAS was repaired and they analyzed the solutions for Cadmium, Lead, Arsenic and Selenium, submitting these results prior to the table of interlaboratory results being submitted to all the participants. Their ICP-AES results are listed under the code 9241 and the GFAAS results are listed under the code 9241A. The original ICP-AES results for Cadmium, Lead, and Arsenic are not included in the calculations of interlaboratory mean and standard deviation.

Laboratory 9241 had intercept problems for all of the Trace Metals except Cadmium. They had a high slope bias for Zinc.

Their performance at the higher concentrations for Lead appears erratic (IADN 3 and IADN4, Figure 11), and may also indicate a negative slope bias. Dilution factors were not reported, but it appears possible that Ampoule IADN3 was not diluted for Lead and analyzed near the top of their analytical range. Ampoule IADN4 may have been diluted for Lead and analyzed at a point in the calibration range where a slope bias was not as pronounced.

Laboratory 9242

Laboratory 9242 was unable to report results for Arsenic and Selenium as their analytical method requires unpreserved samples, and the interlaboratory study ampoules were all acidified with nitric acid.

Laboratory 9242 had intercept problems for all of the Trace Metals except Zinc.

They also noted that they diluted the solutions 1:4 with ultrapure water, to simulate

the same treatment given to precipitation samples. An aliquot of the ultrapure water was analyzed for any background levels of the metals, and the final results were corrected for background levels (uncorrected values were not reported).

Laboratory 9243

No results were received from this participant as they were unable to analyze the aqueous matrix. All Trace Metals analyses done by this laboratory is done using X-Ray Fluorescence on solid matrices.

Laboratory 9244

Laboratory 9244 was the only participant to use Neutron Activation as their analytical method. This procedure is routinely used for the analyses of solid matrices (eg. air filters) and is not easily used for the analysis of aqueous matrices, such as the ampouled solutions used in this study. They were not able to analyze all the solutions for all of the elements in this study.

Laboratory 9244 included a comment with their results indicating that they had difficulty with their analysis for Aluminum because of high blank readings. Their results for Aluminum were excluded from the calculations for the interlaboratory mean, standard deviation and relative standard deviation.

The high bias of their results suggest that the Neutron Activation technique is not appropriate for aqueous samples. They were not able to analyze the low level ampoules for Chromium, but their results for the higher concentration (IADN3 and IADN4) show acceptable agreement with the target. Their results for Copper show a high blank or intercept problem, suggesting that this method, when used on aqueous samples, is not sufficiently sensitive. Their result for the highest Copper concentration (IADN4) showed good agreement with the target. Their Selenium results show a high intercept or blank combined with a negative slope. This again may be a problem associated with using this analytical technique for aqueous samples. Future interlaboratory studies on spiked filters should be a more appropriate way of comparing this participant's performance with other laboratories who are contributing to the IADN database.

Laboratory 9245

Laboratory 9245 noted that the Arsenic and Selenium levels were much higher than their usual working level of 0.1 to 5.0 μg/L. The solutions were diluted 10X for Arsenic and Selenium analysis.

Laboratory 9245 had intercept problems for Arsenic, Copper, and Selenium. The above noted dilutions for Arsenic and Selenium may have magnified this problem. They had a high slope bias for Aluminum. Consistent performance across the concentration range and good agreement with the target was demonstrated for Cadmium, Chromium, Lead and Zinc.

Laboratory 9246

Laboratory 9246 analyzed the samples using two different instruments, ICP-AES and GFAAS. The ICP analysis was a full elemental scan, while the GFAAS results were for Arsenic, Cadmium and Lead only. In the preliminary table of results provided to the participants in November 1992, the ICP Lead results were reported. As samples for

the IADN program are analyzed using GFAAS, the Lead results were replaced with the GFAAS data. The statistical calculations were revised using the GFAAS results.

Laboratory 9246 had problems with their analysis for Zinc, though their accompanying QC data did not indicate a problem. Personal communication with laboratory staff indicated that they had a blank problem for Zinc that resulted in over-correction of the ampouled solutions' results. This resulted in ND values for IADN1 and IADN2, and a very low bias for ampoules IADN3 and IADN4. They requested that their results for Zinc be excluded from the evaluation and they have corrected their analytical protocol to prevent this problem from re-occurring.

Laboratory 9246 had an intercept problem for Aluminum, though they had good agreement with the target at the higher concentrations. They were biased high relative to the target and other participants for Arsenic. Erratic performance for was demonstrated for Selenium. They had generally consistent performance across the concentration range and good agreement with the target for the other four metals in this study.

Laboratory 9247

Laboratory 9247 used two different instruments for their analyses, as noted in Table 2. When reporting their results, they indicated that the solutions in the ampoules were at considerably higher levels than they routinely analyze. Several dilutions were performed (ranging from 1:4 up to 1:499) on all of the ampoules for Cadmium, Lead, and Arsenic analysis. All of the results plus a mean were provided on an accompanying report. The mean results were recorded on the interlaboratory study report form (Appendix 2) and these are the values listed in Table 1. They did not indicate if this was the same procedure that would be used for high level samples. The use of multiple dilutions may have introduced biases that would not be present on undiluted samples.

Laboratory 9247 had a high slope bias for Aluminum. They had an intercept problem for Zinc and Lead (not as severe). They were erratic at the lower concentrations for Cadmium, possibly due to dilution effects. Good performance was demonstrated for the other elements.

Laboratory 9248

Laboratory 9248 was the only participant to use ICP with Mass Spectrometry. They did not report results for Chromium and Selenium.

They demonstrated good performance across the concentration range and were within 10% of the target values for all elements. However, they were biased low relative to the other participants for all elements except Lead. As noted above in the Overall Review, this could lead to biases in the central IADN database. This is a situation where the use of a common reference material by all of the participants would indicate whether Laboratory 9248 really is biased low, or whether the other participants are all biased high.

5   CONCLUSION

The results of this interlaboratory study indicate that the participants generally agree within ±10% of the target for all elements except Aluminum. The lack of sensitivity

for Aluminum analysis suggests that ±20% may be the best agreement achievable at the present time. Within-laboratory performance across the concentration range was very consistent, with one or two individual problems for one or two elements. Intercept problems are the most common source of between-laboratory variability. Individual participants may be biased high or low for one or two individual elements and are recommended to investigate these biases. As between-participant bias may be as high as 20%, the use of a common reference standard could help reduce this bias to 5-10%. This would reduce the potential bias from the contributing laboratories to the central IADN database.

6   REFERENCES

1.   International Joint Commission, United States and Canada; January 1988. *Revised Great Lakes Water Quality Agreement of 1978 as amended by Protocol signed November 18, 1987*.

2.   Canada/U.S. Coordinating Committee on Annex 15; March 1990. *Integrated Atmospheric Deposition Network Implementation Plan*.

3.   *Integrated Atmospheric Deposition Network "STRAW MAN" Quality Assurance Program Plan* (DRAFT); November 1992.

7   APPENDIX 1 - RESULTS AND GRAPHS

TABLE 1: METAL RESULTS IN µg/L

CODE	IADN1	IADN2	IADN3	IADN4	CODE	IADN1	IADN2	IADN3	IADN4
	Al				Cr				
TARGET	80.92	100.6	152.0	225.0	TARGET	9.996	1.999	19.99	79.97
9241	104	113	137	244	9241	8.7	6.0	16.3	82.7
9242	81.2	128.7	176.1	256.9	9242	3.6	<.2	33.2	77.3
9244 *	186	-	243.67	342.33	9244	-	-	25.5	88.15
9245	92	147	195	280	9245	11.5	2.5	22.3	84.6
9246	101	105	164	236	9246	9	ND	21	78
9247	102.90	141.85	196.95	285.15	9247	10.50	2.40	20.20	80.00
9248	71.22	92.24	131.96	200.07	9248	-	-	-	-
MEAN	92.05	121.3	166.8	250.4	MEAN	8.66		23.08	81.79
STD DEV	13.358	21.525	27.93	31.33	STD DEV	3.048		5.787	4.169
n	6	6	6	6	n	5		6	6
REL DEV	14.61%	17.75%	16.74%	12.51%	REL DEV	35.20%		25.07%	5.10%
	Cd				Pb				
TARGET	9.885	1.977	19.77	158.2	TARGET	9.987	19.97	74.90	79.89
9241 [b]	16.4	3.2	27.3	171	9241 [b]	<60	<60	91	<60
9241A	9.49	1.84	17.44	140	9241A	10.22	17.67	60.45	79.0
9242	8.7	1.2	17.8	151.7	9242	11.4	20.5	76.0	80.0
9244	-	-	-	-	9244	-	-	-	-
9245	10.3	2.0	20.6	163	9245	11.2	21.5	81.0	83.4
9246	9.7	2.1	19.2	159	9246 [c]	10	18	69	68
9247	10.98	1.95	18.66	155.10	9247	12.56	22.78	73.38	77.72
9248	9.04	1.78	18.07	143.22	9248	11.28	20.83	72.82	77.96
MEAN	9.702	1.812	18.61	152	MEAN	11.11	20.213	72.108	77.68
STD DEV	0.834	0.321	1.151	8.953	STD DEV	0.922	2.004	6.956	5.170
n	6	6	6	6	n	6	6	6	6
REL DEV	8.60%	17.69%	6.18%	5.89%	REL DEV	8.30%	9.91%	9.65%	6.66%

[a]   Laboratory 9244 reported high blanks for Aluminum. Results are excluded from the calculations of mean and standard deviation. "-" in table indicates that Laboratory 9244 did not report results for that element and/or ampoule.

[b]   Laboratory 9241 had instrument problems during the course of this study. In an attempt to meet the deadline for reporting results, they analyzed the solutions using ICP-AES. They repeated their analysis for Cadmium, Lead, Arsenic and Selenium using Graphite Furnace-AAS (GFAAS). The second set of results are labelled 9241A. The first set of values for these four parameters were not included in the calculations of mean and standard deviation.

[c]   Laboratory 9246 reported Lead results using both ICP-AES and GFAAS. The preliminary table of results had the ICP-AES results, but the IADN samples are analyzed using GFAAS, therefore this table has been revised using the GFAAS results.

TABLE 1: METAL RESULTS IN µg/L

CODE	IADN1	IADN2	IADN3	IADN4	CODE	IADN1	IADN2	IADN3	IADN4
	Cu					**Zn**			
TARGET	9.998	4.999	29.99	79.98	TARGET	10.0	25.0	100	240
9241	13.2	6.4	34.4	87.3	9241	16.8	32.5	116	273
9242	18.2	9.1	32.4	88.2	9242	11.0	30.8	106.8	255.5
9244	16	9.95	37.5	77.333	9244	-	-	-	-
9245	13.1	6.8	34.8	87.3	9245	11.0	25.7	108	248
9246	11	5	32	81	9246	ND	ND	37	171
9247	12.86	6.46	32.38	84.56	9247	17.92	27.08	102.40	244.10
9248	10.94	5.78	27.58	71.42	9248	9.61	24.4	98.9	234.4
MEAN	13.61	7.07	33.01	82.45	MEAN	13.266	28.096	94.85	237.67
STD DEV	2.637	1.792	3.071	6.252	STD DEV	3.801	3.433	28.924	35.128
n	7	7	7	7	n	5	5	6	6
REL DEV	19.37%	25.34%	9.30%	7.58%	REL DEV	28.65%	12.22%	30.49%	14.78%
					MEAN [d]			108.26	254.5
					STD DEV			6.464	14.460
					n [d]			5	5
					REL DEV			5.97%	5.68%
	As					**Se**			
TARGET	10.08	5.04	50.4	161.3	TARGET	9.975	4.988	49.88	141.1
9241 [*]	<60	<60	<60	96	9241 [*]	-	-	-	-
9241A	12.00	4.71	54.42	168.0	9241A	9.17	4.45	45.21	148.0
9242	-	-	-	-	9242	-	-	-	-
9244	-	-	-	-	9244	9.1	7.05	45	130.3
9245	9.0	3.6	50.0	155	9245	8.7	3.6	49.5	150
9246	13	6	59	176	9246	7	4	66	143
9247	10.83	4.78	49.48	168.28	9247	-	-	-	-
9248	9.43	4.53	45.71	147.17	9248	-	-	-	-
MEAN	10.852	4.724	51.72	162.89	MEAN	8.493	4.775	51.428	142.83
STD DEV	1.687	0.856	5.108	11.580	STD DEV	1.016	1.556	9.934	8.854
n	5	5	5	5	n	4	4	4	4
REL DEV	15.55%	18.13%	9.88%	7.11%	REL DEV	11.97%	32.58%	19.32%	6.20%

[d]   Mean, Standard Deviation and Relative Deviation recalculated excluding Laboratory 9246.

[*]   Laboratory 9241 had instrument problems during the course of this study. In an attempt to meet the deadline for reporting results, they analyzed the solutions using ICP-AES. They repeated their analysis for Cadmium, Lead, Arsenic and Selenium using Graphite Furnace-AAS (GFAAS). The second set of results are labelled 9241A. The first set of values for these four parameters were not included in the calculations of mean and standard deviation.

TABLE 2: INSTRUMENTATION OF PARTICIPANTS

| ID Code	Instrumentation
9241	Thermo-Jarrell Ash ICP-AES, Vacuum, direct reader
9241A	Instrumentation Laboratory Video 22 AAS-GF
9242	ICP, ARL 3580
9244	Neutron Activation
9245	ICP, ARL 3580; direct aspiration for Al, Cd, Cr, Cu, Pb & Zn; hydride formation for As & Se
9246	GFAAS for As, Cd & Pb ICP-AES for Al, Cr, Cu, Se & Zn
9247	Perkin Elmer 5000 AAS for As, Cd, Cr & Pb Jarrell Ash ICP for Al, Cu & Zn
9248	ICP-MS
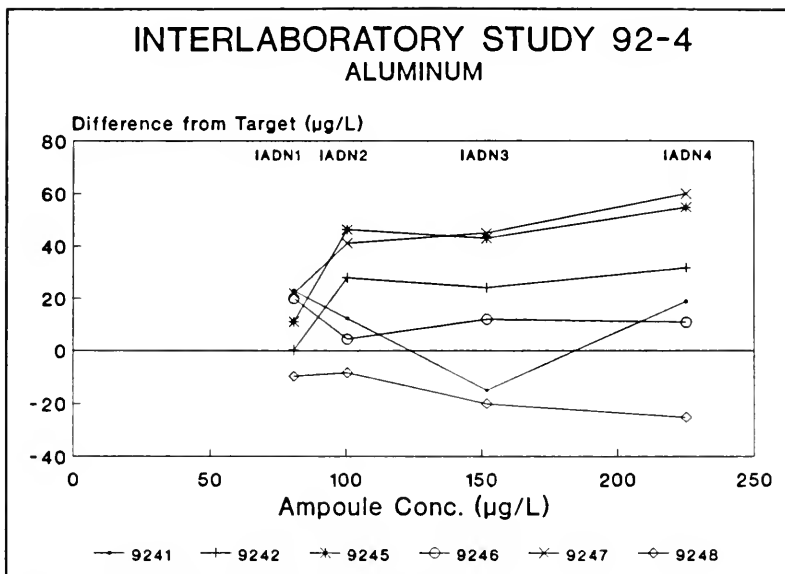
Figure 1 - Absolute Difference from Target
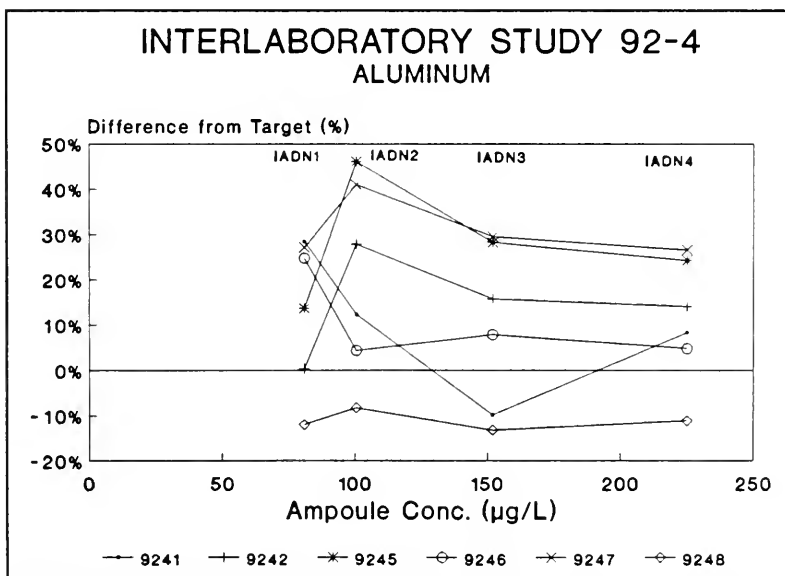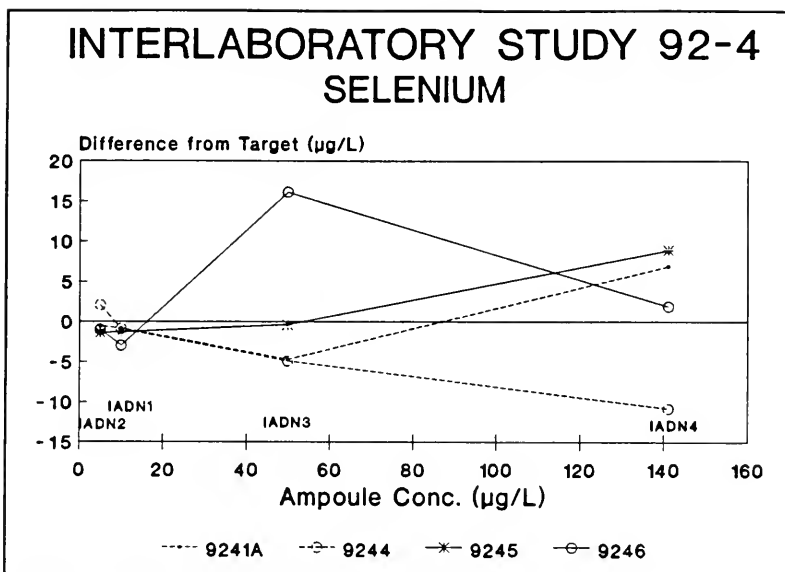

Figure 2 - Percent Difference from Target
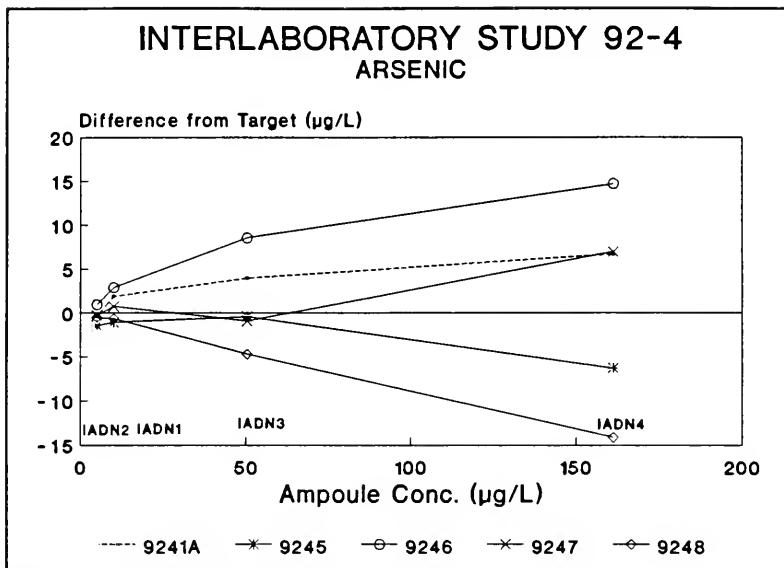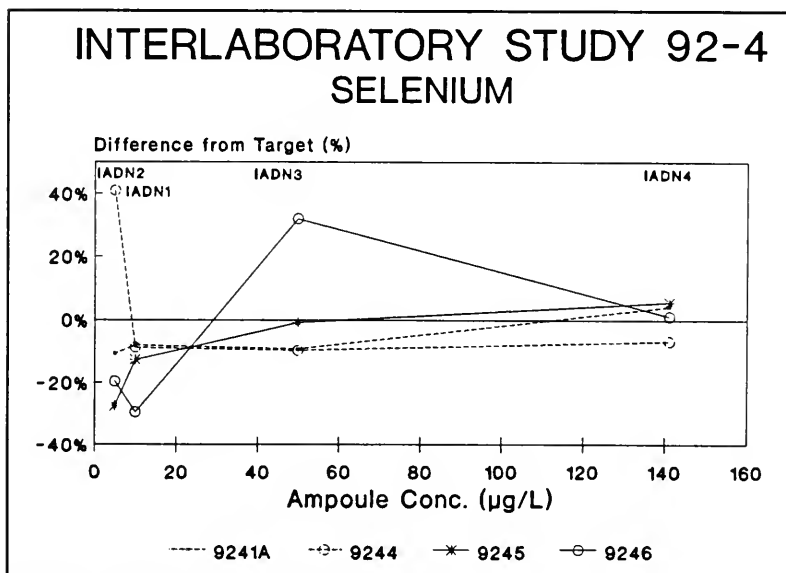
Figure 3 - Absolute Difference From Target
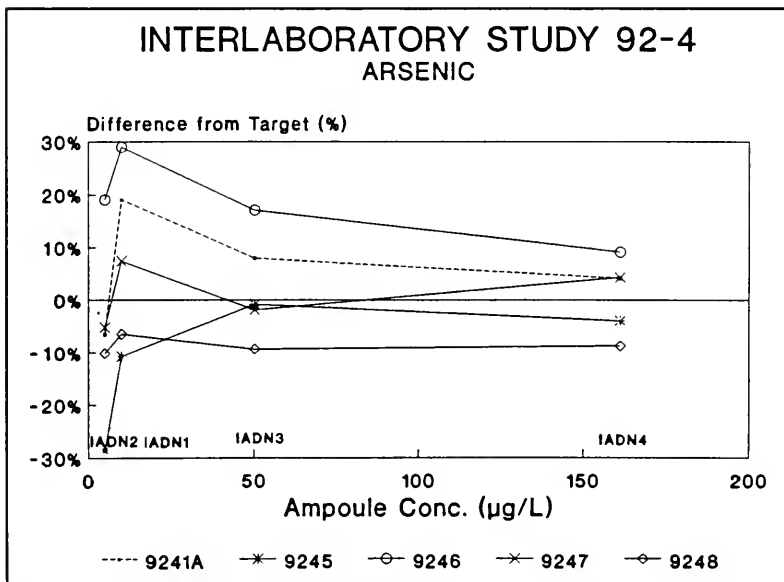
Figure 4 - Percent Difference from Target
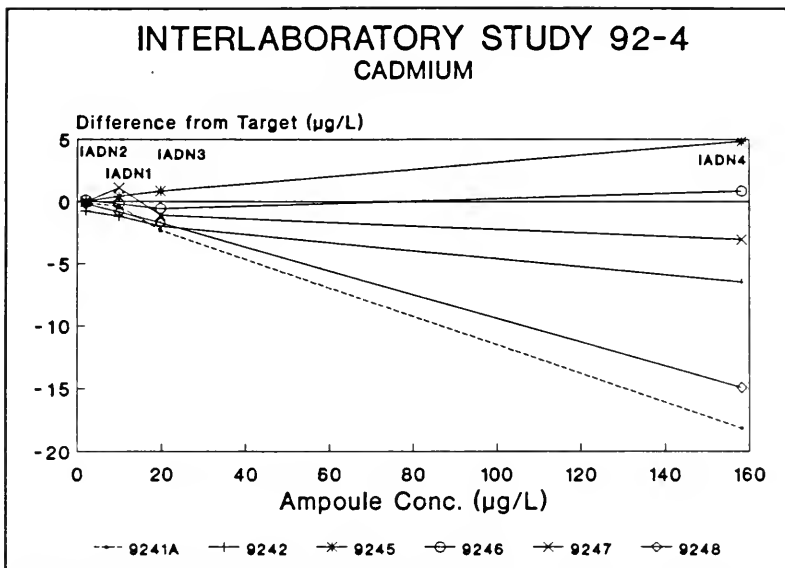
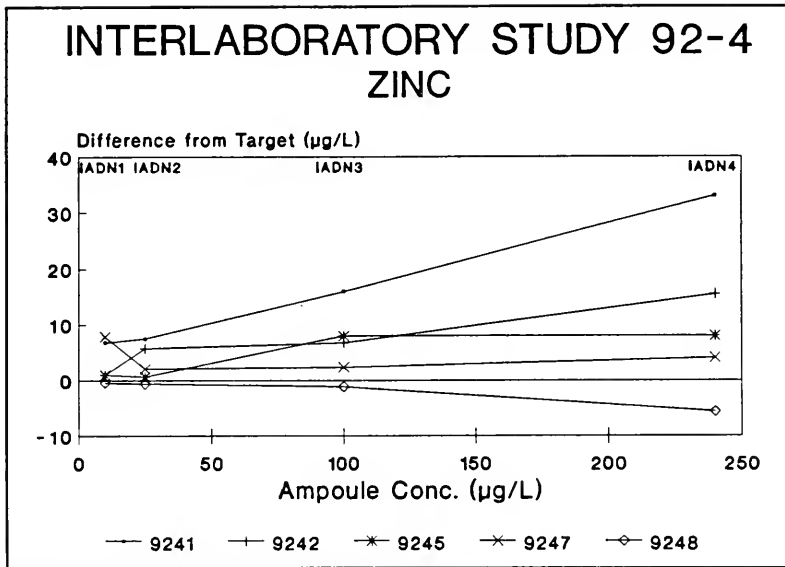Figure 5 - Absolute Difference from Target
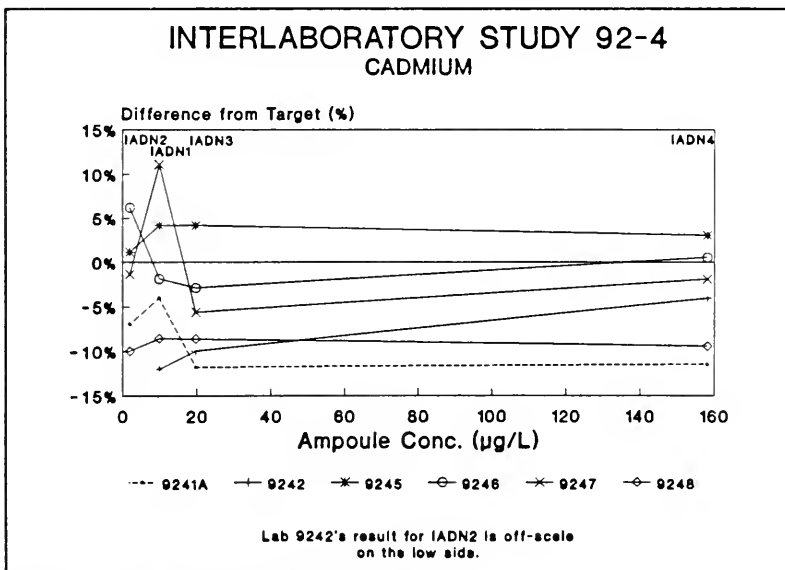
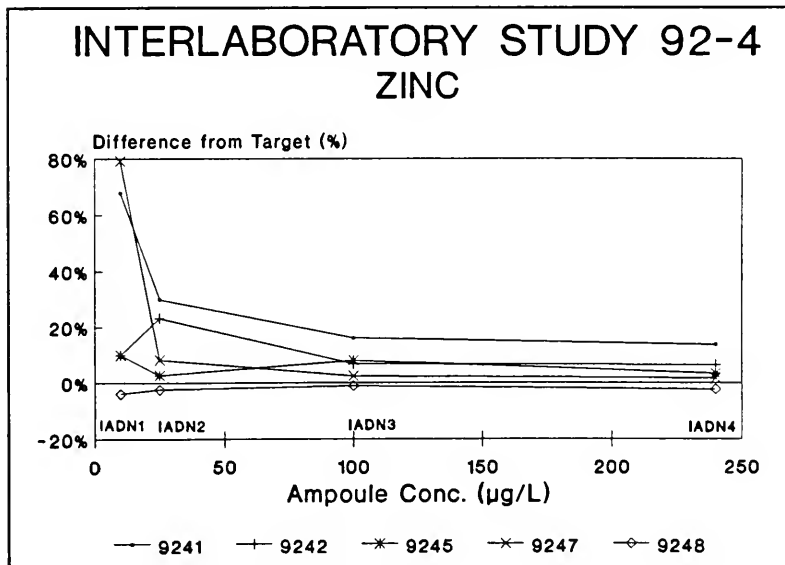Figure 6 - Percent Difference from Target
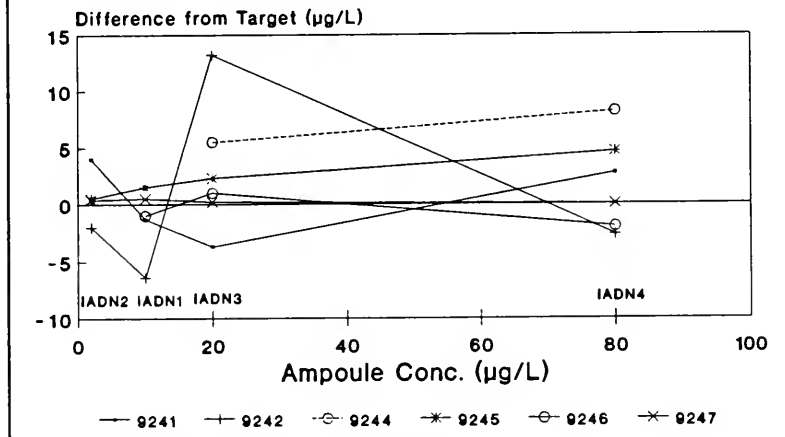
Figure 7 - Absolute Difference from Target
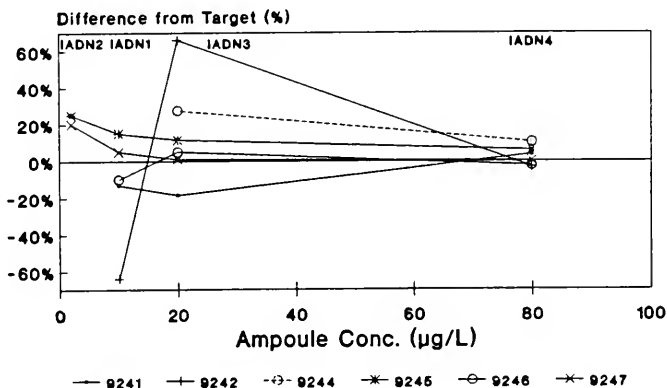
Figure 8 - Percent Difference from Target
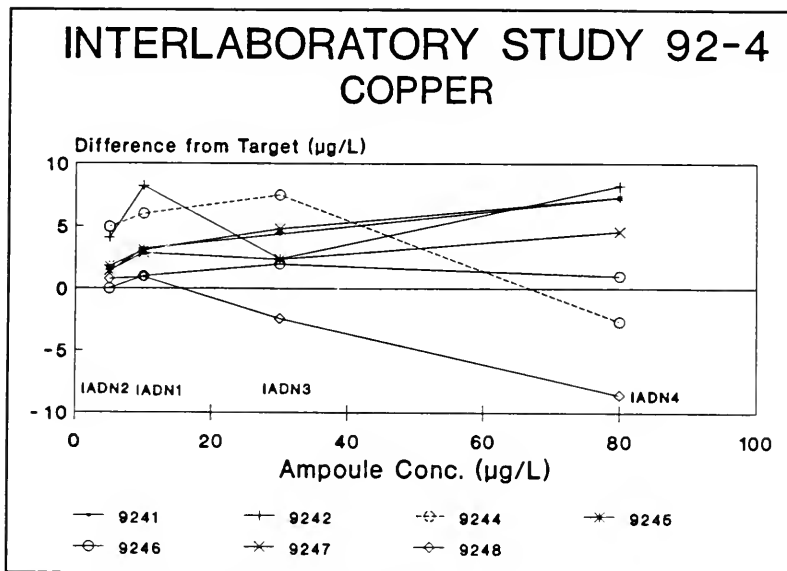
Figure 9 - Absolute Difference from Target
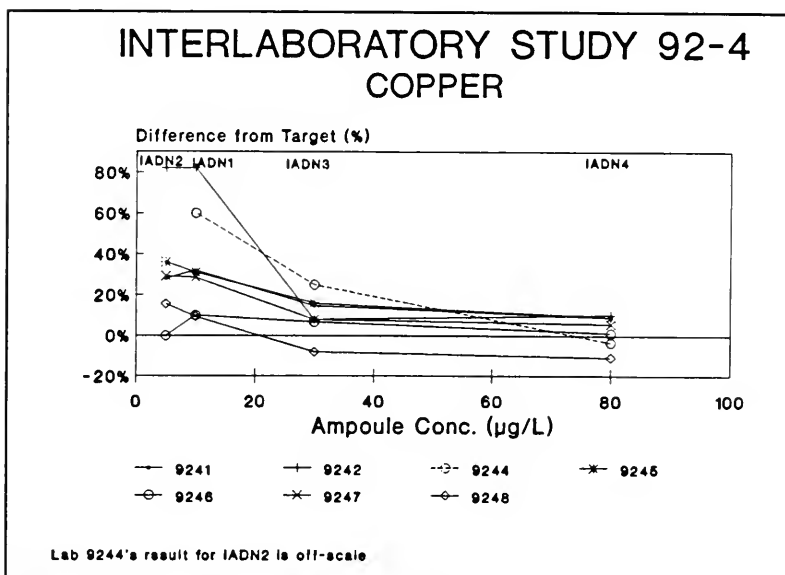
Figure 10 - Percent Difference from Target
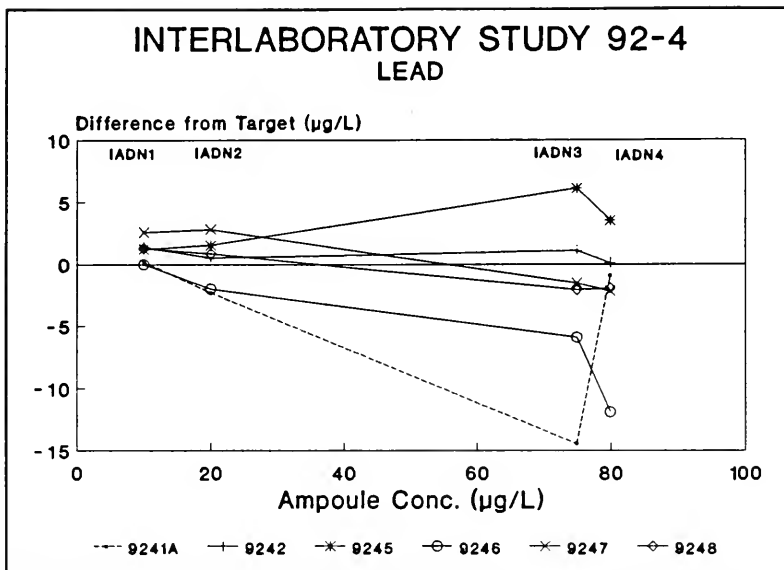
Figure 11 - Absolute Difference from Target
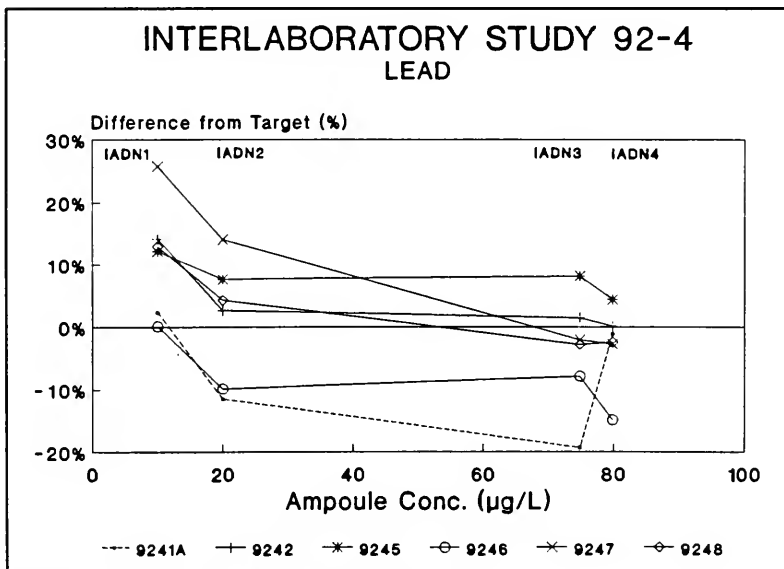
Figure 12 - Percent Difference from Target

Figure 13 - Absolute Difference from Target

Figure 14 - Percent Difference from Target

Figure 15 - Absolute Difference from Target

Figure 16 - Percent Difference from Target

8   APPENDIX 2 - PARTICIPANTS AND CORRESPONDENCE

List of Participants

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July 13, 1992

Dear Interlaboratory Study 92-4 Participant,

Please find enclosed four 50 mL ampoules for the analysis of metals. The ampoules are labelled IADN1, IADN2, IADN3, and IADN4. If you are missing any of the ampoules or they have broken in transit, please contact Sathi Selliah at (416) 235-5700 immediately for replacement.

The ampoules are ready for direct instrumental analysis. Break open the ampoule on the scored mark and transfer the contents to the appropriate sample container for your analytical system. No dilutions should be required, but if you do so, please mark the dilution factor used on the accompanying report form. All the ampoules contain the following metals: Aluminum, Chromium, Copper, Zinc, Arsenic, Selenium, Cadmium and Lead.

Please report all results on the accompanying form by August 7, 1992.

Thank you for your participation in this study.

Your identification code is:

Sylvia Cussion
Laboratory Quality Audit Scientist
(416) 235-5842
FAX (416) 235-6110

INTERLABORATORY STUDY 92-4

METALS FOR THE INTEGRATED ATMOSPHERIC DEPOSITION NETWORK

Identification Code:

Units:

Element	IADN1	IADN2	IADN3	IADN4
Al				
Cd				
Cr				
Cu				
Pb				
Zn				
As				
Se				

INSTRUMENT USED FOR ANALYSIS:

Quality Management Office

November 4, 1992

Dear Participant of Interlaboratory Study 92-4,

Please find enclosed the table of results from Interlaboratory Study 92-4. If there are any transcription errors, please contact me at (416) 235-5842.

As originally indicated in the initial study outline, there will be three phases for Interlaboratory Study 92-4. The target date for the submission of Phase 2 samples (ampouled solutions) is mid-January 1993. Exact details will be provided in December 1992.

Your identification code is:

Sincerely,

Sylvia Cussion
Laboratory Quality Audit Scientist
(416) 235-5842

9   APPENDIX 3 - INTERPRETATION OF BIASES IN DIFFERENCE PLOTS

Interlaboratory study results may be evaluated by comparing the difference from target (D) to the target or consensus value (X). This may be graphically represented with the Difference (D) on the vertical axis and the Target or consensus value (X) on the horizontal axis. By joining the individual points for each participant in order of increasing concentration, imprecision (squiggle in the line) versus bias or curvature (location of line relative to its expected position) may be demonstrated.

The precision envelope for the difference plots may be described by the following equation:

$$D = B_i + B_s {}^*C \pm (DL + f {}^*C)$$

where: D   Difference from target B_i Intercept Bias
          C   Concentration B_s Slope Bias
          DL   Detection Limit   f   Fluctuation factor

The fluctuation factor (f) for Trace Metals is usually 5-10%. Data users' needs may determine how large a value for f is acceptable.

If there are no biases present (B_i and B_s = 0), the shape is symmetrical to and centred on the target line. Measurement differences among participating laboratories in an interlaboratory study should be attributable only to random fluctuation. An example using DL = 5 μg/L and f = 10% is given in Figure 17.

When an intercept bias is present, the envelope shifts in the direction of the bias. If this shift exceeds the Method Detection Limit (MDL), this becomes a matter of concern for the analyst. An example with B_i = -5 μg/L is given in Figure 19.

When a slope bias is present, the envelope broadens in the direction of the bias as concentration increases. Then this bias exceeds the MDL + 10% concentration, it becomes a matter of concern for the analyst. An example of B_s = +10% is given in Figure 21.

Most interlaboratory study data sets will show a combination of slope and intercept biases among the participants. The precision envelope changes according the magnitude of both effects. An example using B_i = -5 μg/L and B_s = +10% is given in Figure 23.

The results may also plotted using the relative difference (R) on the vertical axis. the precision envelope flares dramatically as the concentration approaches zero. This type of plot tends towards an exaggerated impression of acceptable variability at the bottom end and may mask biases at higher concentration levels. However it can be useful when describing the range of performance among a group of participants. The above examples that were presented using concentration units (absolute scale) are also presented using a relative scale (Figures 18, 20, 22 and 24).

REFERENCE

King, D.E.; July 1993; *Interpretation of Interlaboratory Comparison (Round-Robin) Data*; Internal Report, Ministry of Environment and Energy, Laboratory Services Branch; Draft.
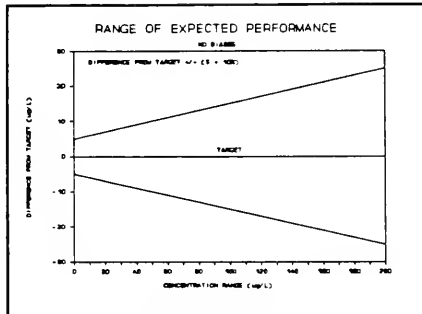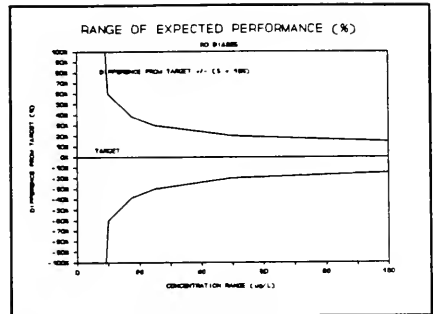
Figure 17 - Absolute Scale
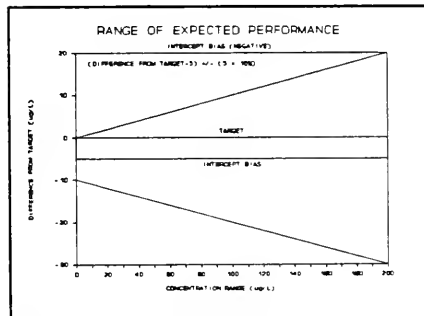

Figure 18 - Relative (%) Scale

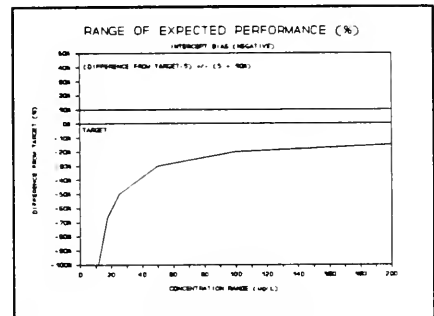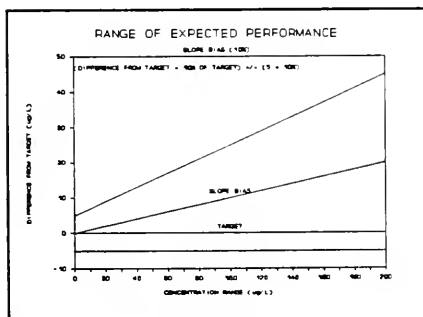**Figure 19 - Absolute Scale**

Figure 20 - Relative (%) Scale
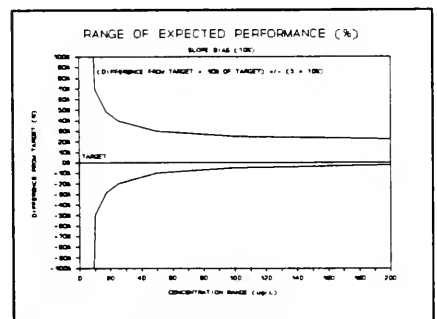

Figure 21 - Absolute Scale
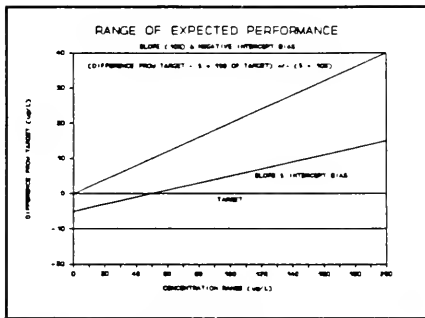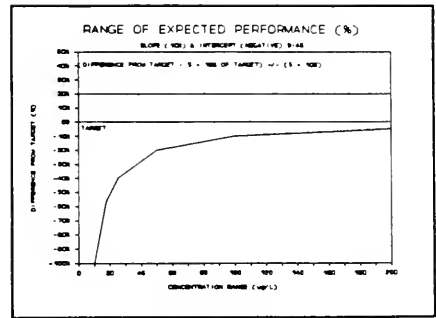

Figure 22 - Relative (%) Scale

Figure 23 - Absolute Scale

Figure 24 - Relative (%) Scale